

# Preparation of Isotacticity-Rich Poly(*tert*-Butyl Vinyl Ether) by the Cationic Polymerization of *tert*-Butyl Vinyl Ether with Dimethyl[*rac*-ethylenebis(indenyl)]zirconium and Tri(pentafluorophenyl)borane

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**ABSTRACT:** *tert*-Butyl vinyl ether (tBVE) was polymerized with the catalyst dimethyl[*rac*-ethylenebis(indenyl)]zirconium (ansa-zirconocene) with tri(pentafluorophenyl)borane [B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] as a cocatalyst. The effects of various polymerization conditions, such as the polymerization time, type of polymerization solvent, polymerization temperature, and catalyst concentration, on the conversion of tBVE into poly(tBVE), its molecular weight and molecular weight distribution, and its stereoregularity were investigated. The maximum conversion of tBVE into poly(tBVE) was over 90% at a polymerization temperature of -30°C with an ansa-zirconocene and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> concentration of 3.0 × 10<sup>-7</sup> mol/mol of tBVE, respectively. The number-average molecular weights of poly(tBVE) ranged from approximately 14,000 to 20,000, with a lower polydispersity index (weight-

average molecular weight/number-average molecular weight) ranging from 1.48 to 1.77, at all polymerization temperatures. The number-average molecular weight of poly(tBVE) increased with decreases in the polymerization temperature and catalyst concentration. The mm triad sequence fraction of poly(tBVE) polymerized with ansa-zirconocene/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> at -30°C was much higher than that of poly(tBVE) polymerized with the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> catalyst at -30°C, and this indicated that the ansa-zirconocene/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> catalyst system affected the isospecific polymerization of tBVE. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1487–1492, 2008

**Key words:** tBVE; cationic polymerization; ansa-zirconocene/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>

## INTRODUCTION

Generally, poly(vinyl alcohol)s (PVAs) are obtained by the saponification of a precursor such as poly(vinyl ester) or poly(vinyl ether), and they are classified into three types—*isotactic*, *atactic*, and *syndiotactic*—according to the stereoregularity of hydroxyl groups. It is well known that *atactic* or *syndiotactic* PVA is synthesized by free-radical polymerization (bulk, solution, emulsion, and suspension) of a precursor and resultant saponification.<sup>1–11</sup> However, it is very difficult to obtain *isotactic* PVA by free-radical polymerization. Thus, to prepare PVA having high *isotacticity*, it is necessary to use a special polymerization adapting an ion catalyst, not general free-radical polymerization.

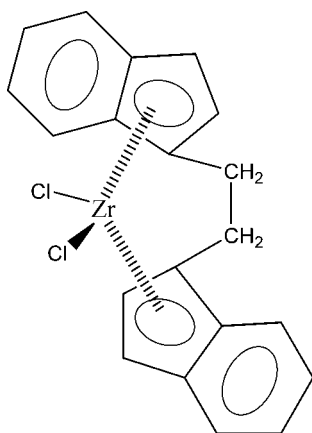
It is well known that vinyl ethers such as *tert*-butyl vinyl ether (tBVE), benzyl vinyl ether (BzVE), isobutyl vinyl ether (iBVE), and trimethylsilyl vinyl ether have

been studied as starting monomers to obtain stereoregular PVA.<sup>12–14</sup> In particular, there are many reports about the stereoregular polymerization of tBVE with homogeneous cationic catalysts such as modified Ziegler-type catalysts (VCl<sub>4</sub>-Et<sub>3</sub>Al and TiCl<sub>4</sub>-Et<sub>3</sub>Al mixtures) and boron trifluoride diethyl etherate (BF<sub>3</sub> · OEt<sub>2</sub>).<sup>13–15</sup> Murahashi et al.<sup>15</sup> successfully prepared *isotacticity*-rich PVA by the cationic polymerization of BzVE followed by hydrolysis with hydrogen bromide. Ohgi and Sato<sup>13,14</sup> obtained highly *isotactic* PVA using the cationic polymerization of tBVE with BF<sub>3</sub> · OEt<sub>2</sub>. They also studied the polymerization of tBVE and BzVE with heterogeneous catalysts such as modified Ziegler-type (Vandenberg-type) catalysts and metal sulfate-sulfuric acid complexes.

The metallocene catalysts have made possible the synthesis of *isotactic* and *syndiotactic* polypropylene<sup>16,17</sup> as well as *syndiotactic* polystyrene,<sup>18</sup> beside the achievement of order in the structure, it is also possible to control the molecular weight in the polymer.<sup>19,20</sup> Wang and Baird<sup>21</sup> studied vinyl ether polymerization with the Cp\*TiMe<sub>3</sub> (Cp\* = η<sup>5</sup>-pentamethylcyclopentadienyl)/tri(pentafluorophenyl)borane [B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] catalytic system. The polymerization of iBVE in CH<sub>2</sub>Cl<sub>2</sub> at -78°C produced a poly(iBVE) with a number-average molecular weight (*M<sub>n</sub>*) of

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**Scheme 1** Schematic representation of the ansa-zirconocene catalyst.

$4.1 \times 10^{-4}$  g/mol and a relatively high polydispersity [weight-average molecular weight/number-average molecular weight ( $M_w/M_n$ ) = 2.4]; the polymer contained a syndiotactic fraction of 56% and an isotactic fraction of 44%. Dimethyl[*rac*-ethylenebis(indenyl)]zirconium (ansa-zirconocene; Scheme 1), one of the metallocene catalysts, has an ethylene bridge that links the top and bottom big and bulky indenyl ligands. Therefore, because of the big and bulky indenyl ligands, monomers react with ansa-zirconocene on only one side.

Therefore, in this study, to increase the isotacticity and to obtain a narrow molecular weight distribution, tBVE was polymerized with ansa-zirconocene/ $B(C_6F_5)_3$  under various polymerization conditions.

## EXPERIMENTAL

### Materials

All operations were performed under purified nitrogen with general Schlenk techniques with a double-manifold vacuum line.<sup>22</sup> The monomer tBVE (98%; Aldrich, Co, St. Louis, MO) was distilled from  $CaH_2$  during overnight. To remove surviving oxygen in tBVE, freezing and thawing under reduced pressure of nitrogen were conducted. The purified tBVE was stored at  $-20^\circ C$  under nitrogen. Ansa-zirconocene was methylated by methylmagnesium bromide ( $CH_3MgBr$ ) from dichloro[*rac*-ethylenebis(indenyl)]zirconium (Aldrich) in toluene.<sup>21</sup> First, dichloro[*rac*-ethylenebis(indenyl)]zirconium and  $CH_3MgBr$  were added to toluene at  $-78^\circ C$ . The mixture was left to reach room temperature with stirring for 4 h and then was filtered. To obtain a more purified product, ansa-zirconocene was obtained by recrystallization from toluene at  $-78^\circ C$ .  $B(C_6F_5)_3$ , purchased from Aldrich, was used without further purification. Solvents, such as toluene, hexane, and tetrahydrofuran

(THF), were purified and dehydrated carefully with sodium and benzophenone before use.

### Polymerization

The polymerization of tBVE was carried out with ansa-zirconocene in several solvents such as toluene, hexane, and THF at various temperatures. The Schlenk flask was passed under dry nitrogen, and then the solvent, catalyst, and cocatalyst were introduced with a syringe, respectively. After the catalyst and cocatalyst were mixed at a given temperature, the monomer was slowly added with a syringe for a given time. Once the reaction time was reached, the polymerization was terminated by the addition of a small amount of methanol. The mixture was then poured into a large amount of methanol, and the precipitated polymer was washed several times with methanol and dried *in vacuo*.

### Molecular weight measurements

The  $M_n$ ,  $M_w$ , and polydispersity ( $M_w/M_n$ ) values of poly(tBVE) were measured by gel permeation chromatography at  $35^\circ C$  in THF at a flow rate of 1.0 mL/min. The  $M_n$  and  $M_w/M_n$  values of the polymers were calculated from their chromatograms on the basis of polystyrene standards.

### NMR analysis

The stereoregularity of poly(tBVE) was determined by means of  $^{13}C$ -NMR spectroscopy. The measurement was performed on a Bruker 500-MHz spectrometer (Bruker, Karlsruhe, Germany) in  $CDCl_3$  at room temperature.

## RESULTS AND DISCUSSION

The polymerization of tBVE was carried out with ansa-zirconocene catalysts at various temperatures in toluene, THF, and hexane, respectively. The parameters for the polymerization of tBVE and the polymerization results of this study are summarized in Tables I and II, respectively. To compare the ansa-zirconocene catalyst system and boron compound, we also tried the polymerization of tBVE with only the boron compound catalyst in toluene. The tBVE monomer was polymerized at different temperatures (from  $-10$  to  $-70^\circ C$ ) by the ansa-zirconocene catalyst system; the maximum conversion of monomer to polymer was 92% at  $-30^\circ C$ . The  $M_n$  values of poly(tBVE) were about 14,000–20,000 g/mol with a relatively narrow polydispersity of 1.48–1.77 at various polymerization temperatures. It is well known that aromatic groups of the solvent, additive, monomer, or polymer interact with the growing chain in carbocationic polymerization.<sup>23</sup> In the case of a highly

**TABLE I**  
Parameters for the Polymerization of tBVE

Type of solvent
Toluene
THF
Hexane
Catalyst and cocatalyst concentration
$6.0 \times 10^{-7}$ mol/mol of tBVE
$3.0 \times 10^{-7}$ mol/mol of tBVE
$1.5 \times 10^{-7}$ mol/mol of tBVE
Temperature
-10°C
-30°C
-50°C

polar solvent such as THF, the monomer and ansa-zirconocene catalyst did not react, whereas the reactivity of the monomer and ansa-zirconocene catalysts increased in a low-polarity solvent such as hexane or toluene. As in the usual cationic polymerization, the meso contents increased with decreasing solvent polarity.<sup>24</sup> Thus, we concluded that toluene is one of the best solvents for the polymerization of tBVE with the ansa-zirconocene catalyst system. It has been reported that toluene is one of the best solvents possible for obtaining a highly isotactic polymer in the polymerization of tBVE with  $\text{BF}_3 \cdot \text{OEt}_2$ .<sup>14</sup> In particular, poly(tBVE) was obtained from the polymerization of tBVE with only  $\text{B}(\text{C}_6\text{F}_5)_3$  (cocatalyst). With an ansa-zirconocene catalyst system at -30°C, the polymer yield and molecular weight were 92% and 14,104 g/mol, respectively. In contrast, with only  $\text{B}(\text{C}_6\text{F}_5)_3$  at -30°C, the polymer yield and molecular weight were 60% and 7027 g/mol, respectively. On the basis of these results, it may be suggested that the active site of  $\text{B}(\text{C}_6\text{F}_5)_3$  affected the polymerization of tBVE with the ansa-zirconocene catalyst system.

Figures 1 and 2 show the effects of the polymerization temperature and catalyst concentration on

the activity of tBVE polymerization with ansa-zirconocene/ $\text{B}(\text{C}_6\text{F}_5)_3$ . The polymerization of tBVE with ansa-zirconocene/ $\text{B}(\text{C}_6\text{F}_5)_3$  was quickly started at all temperatures and at all catalyst concentrations. After that, the activity of the catalyst rapidly decreased. In the case of the polymerization of various alkyl vinyl ethers with a Lewis acid, generally, the vinyl ethers with a branched substituent (isopropyl vinyl ether, tBVE, and iBVE) were polymerized much faster than those with a linear substituent (*n*-propyl vinyl ether and *n*-butyl vinyl ether). These results probably occurred because when the monomer's alkyl group was less bulky, the catalyst could interact (form a complex) more easily and was thus less available for the dissociation of the terminal bond into the growing cation.<sup>25,26</sup> Therefore, it is supposed that the polymerization of tBVE with ansa-zirconocene/ $\text{B}(\text{C}_6\text{F}_5)_3$  was a fast reaction because of the strong interaction between tBVE with a branched substituent and ansa-zirconocene/ $\text{B}(\text{C}_6\text{F}_5)_3$ .

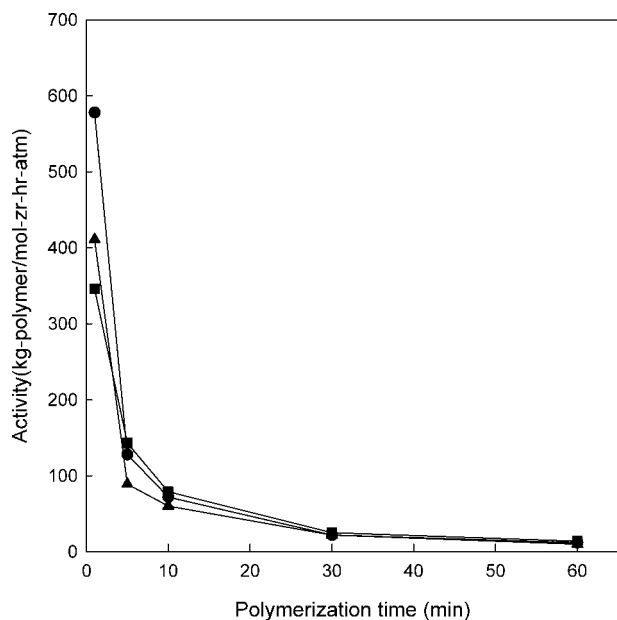
The time-conversion curves with the polymerization temperature and catalyst concentration for the polymerization of tBVE with ansa-zirconocene/ $\text{B}(\text{C}_6\text{F}_5)_3$  are presented in Figures 3 and 4, respectively. It is well known that the stability of the propagating species in cationic polymerization suppresses chain-transfer, termination, and other side reactions.<sup>13</sup> The maxima of the ultimate conversion and the rate of polymerization of tBVE with ansa-zirconocene/ $\text{B}(\text{C}_6\text{F}_5)_3$  were obtained at a polymerization temperature of -30°C. The ultimate conversion was also increased from 60 to 90% as the polymerization temperature increased from -50 to -30°C. On the other hand, as the polymerization temperature increased from -30°C to -10°C, the ultimate conversion decreased from 90 to 80%, as shown in Figure 3. This might be explained by the fact that the activity of the cationic propagating species is maintained

**TABLE II**  
Characterization of Poly(tBVE)s Prepared with Ansa-Zirconocene in Several Solvents

No.	Monomer (mL)	Temperature (°C)	Solvent	Polymer yield (%)	Poly(tBVE)		
					$M_n$	$M_w$	$M_w/M_n$
1	1	-70	Toluene	65	19,186	28,395	1.48
2	1	-60	Toluene	69	18,068	28,186	1.56
3	1	-50	Toluene	76	17,239	26,273	1.53
4	1	-40	Toluene	83	15,701	23,733	1.51
5	1	-30	Toluene	92	14,104	22,036	1.56
6	1	-20	Toluene	75	16,523	29,202	1.77
7	1	-10	Toluene	62	14,236	23,103	1.62
8	2	-20	Toluene	45	17,679	27,131	1.53
9	2	-20	Hexane	73	13,220	19,806	1.50
10	2	-20	THF	—	—	—	—
11	1	20	THF	—	—	—	—
12 <sup>a</sup>	1	-30	Toluene	60	7027	10,604	1.51

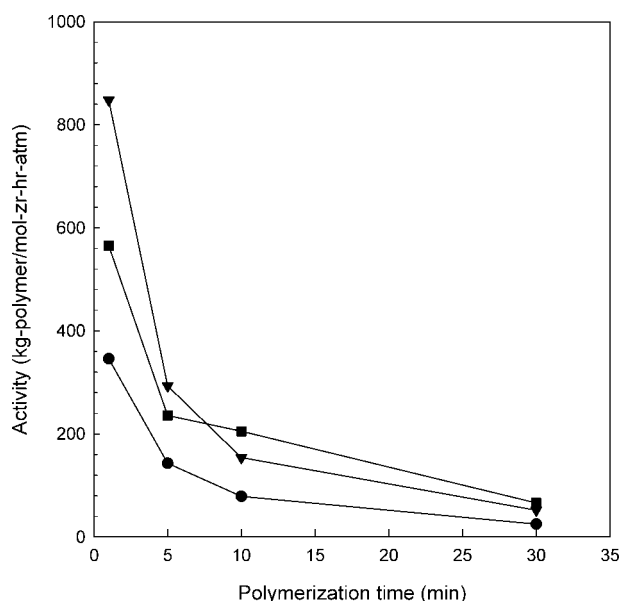
The catalyst and cocatalyst concentration was  $6.0 \times 10^{-7}$  mol/mol of tBVE; the polymerization time was 1 h.

<sup>a</sup> Only  $\text{B}(\text{C}_6\text{F}_5)_3$  (without ansa-zirconocene).

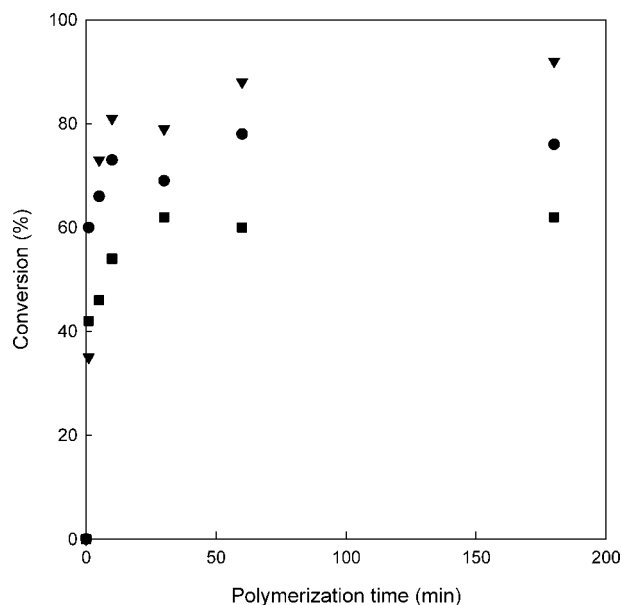


**Figure 1** Effect of the polymerization temperature on the activity of tBVE polymerization with ansa-zirconocene/ $B(C_6F_5)_3$ : (●)  $-10^\circ C$ , (■)  $-30^\circ C$ , and (▲)  $-50^\circ C$ .

when the reaction temperature is kept at  $-30^\circ C$  and the ultimate conversion and rate of polymerization decrease because of the slower polymerization rate at the lower polymerization temperature of  $-50^\circ C$  and instability of the maintenance of the activity of the catalysts at the higher temperature of  $-10^\circ C$ . The effect of the catalyst concentration on the conversion of tBVE into poly(tBVE) cationi-

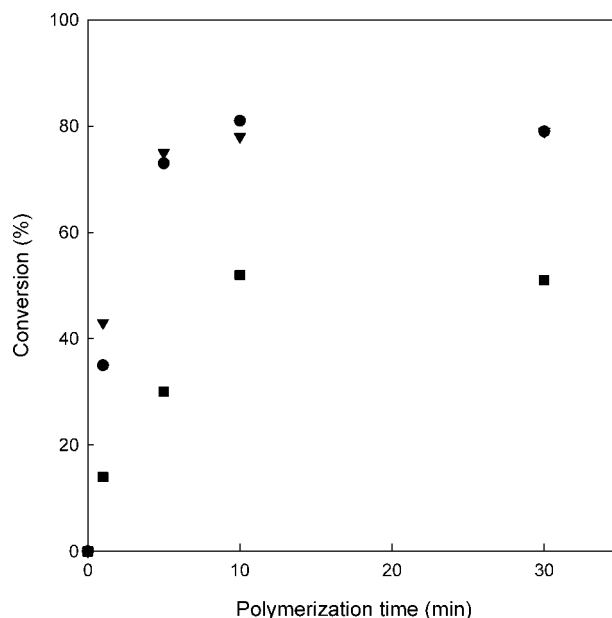


**Figure 2** Effect of the catalyst concentration on the activity of tBVE polymerization with ansa-zirconocene/ $B(C_6F_5)_3$ : (●)  $6.0 \times 10^{-7}$ , (▼)  $3.0 \times 10^{-7}$ , and (■)  $1.5 \times 10^{-7}$  mol/mol of tBVE.

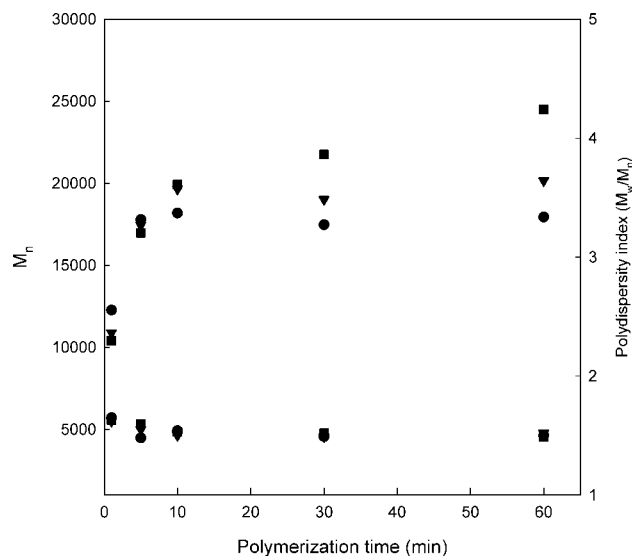


**Figure 3** Time-conversion curves with different temperatures for the polymerization of tBVE with ansa-zirconocene/ $B(C_6F_5)_3$ : (●)  $-10^\circ C$ , (▼)  $-30^\circ C$ , and (■)  $-50^\circ C$ .

cally polymerized at  $-30^\circ C$  is shown in Figure 4. The conversion rate increased as the catalyst concentration increased. The ultimate conversions were obtained at the catalyst concentrations of  $6.0 \times 10^{-7}$  and  $3.0 \times 10^{-7}$  mol/mol of tBVE. Thus, the catalyst concentration of  $3.0 \times 10^{-7}$  mol/mol of tBVE is a suitable one for producing poly(tBVE) with a high yield.

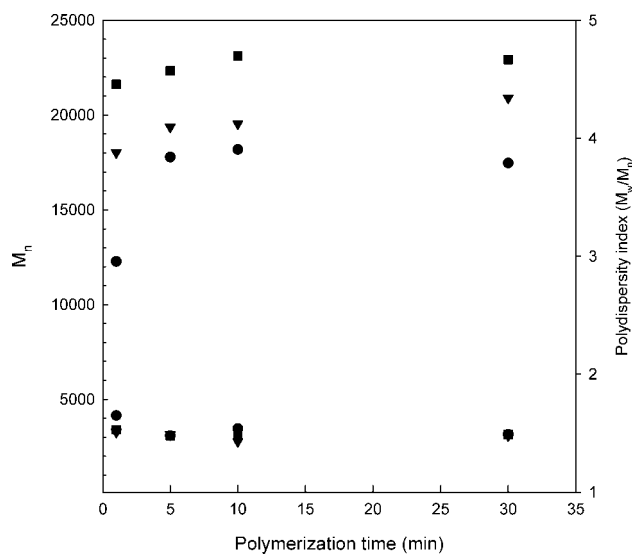


**Figure 4** Time-conversion curves with different catalyst concentrations for the polymerization of tBVE with ansa-zirconocene/ $B(C_6F_5)_3$ : (●)  $6.0 \times 10^{-7}$ , (▼)  $3.0 \times 10^{-7}$ , and (■)  $1.5 \times 10^{-7}$  mol/mol of tBVE.



**Figure 5** Effect of the polymerization temperature on the  $M_n$  and polydispersity index values of poly(tBVE) prepared by the polymerization of tBVE with ansa-zirconocene/ $B(C_6F_5)_3$ : (●)  $-10^\circ\text{C}$ , (▼)  $-30^\circ\text{C}$ , and (■)  $-50^\circ\text{C}$ . The upper symbols represent  $M_n$ , and the bottom symbols represent the polydispersity index.

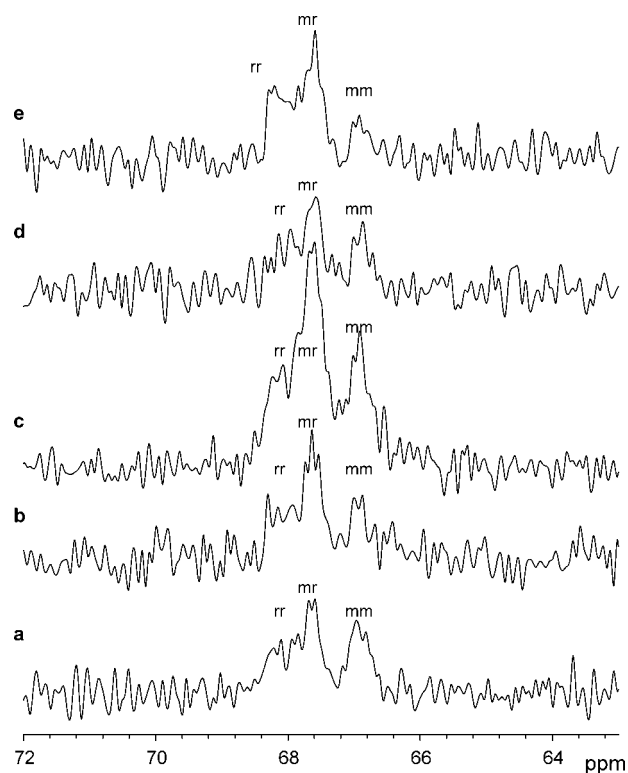
The effect of the polymerization temperature on the molecular weight and polydispersity of poly(tBVE) prepared by the polymerization of tBVE with ansa-zirconocene/ $B(C_6F_5)_3$  is shown Figures 5 and 6, respectively. The molecular weight of poly(tBVE) increased with a decrease in the polymerization temperature, and a narrow molecular weight distribu-



**Figure 6** Effect of the catalyst concentration on the  $M_n$  and polydispersity index values of poly(tBVE) prepared by the polymerization of tBVE with ansa-zirconocene/ $B(C_6F_5)_3$ : (●)  $6.0 \times 10^{-7}$ , (▼)  $3.0 \times 10^{-7}$ , and (■)  $1.5 \times 10^{-7}$  mol/mol of tBVE. The upper symbols represent  $M_n$ , and the bottom symbols represent the polydispersity index.

tion was obtained from 1.4 to 1.6 at all temperatures. The molecular weight of poly(tBVE) increased with decreasing catalyst concentration, indicating lower probabilities of chain terminations.

Finally, to check the stereoregularity of poly(tBVE) obtained under various polymerization conditions, we analyzed poly(tBVE) specimens with  $^{13}\text{C}$ -NMR spectroscopy in  $\text{CDCl}_3$  at room temperature. Figure 7 shows the zoomed  $^{13}\text{C}$ -NMR spectra of poly(tBVE) polymerized in toluene at various polymerization temperatures and catalyst concentrations. Generally, the dyad tacticity of poly(tBVE) is calculated from the triad data measured from the main-chain methines around 66–70 ppm due to split main-chain methine signals by the steric structures.<sup>26,27</sup> In Figure 7, the mm sequence fraction of poly(tBVE) polymerized at  $-30^\circ\text{C}$  is richer than that of poly(tBVE) polymerized at  $-70^\circ\text{C}$ , and the catalyst concentration did not affect the stereoregularity of poly(tBVE). In particular, the rr sequence fraction of poly(tBVE) polymerized with only  $B(C_6F_5)_3$  at  $-30^\circ\text{C}$  was richer than the mm sequence fraction, and this indicated that isotacticity-rich poly(tBVE) could not be formed because of the absence of ansa-zirconocene.



**Figure 7**  $^{13}\text{C}$ -NMR spectra of poly(tBVE) obtained under various polymerization conditions: (a) ansa-zirconocene/ $B(C_6F_5)_3$  of  $6.0 \times 10^{-7}$  mol/mol of tBVE at  $-30^\circ\text{C}$ , (b) ansa-zirconocene/ $B(C_6F_5)_3$  of  $6.0 \times 10^{-7}$  mol/mol of tBVE at  $-70^\circ\text{C}$ , (c) ansa-zirconocene/ $B(C_6F_5)_3$  of  $1.5 \times 10^{-7}$  mol/mol of tBVE at  $-30^\circ\text{C}$ , (d) ansa-zirconocene/ $B(C_6F_5)_3$  of  $3.0 \times 10^{-7}$  mol/mol of tBVE at  $-30^\circ\text{C}$ , and (e) only  $B(C_6F_5)_3$  of  $6.0 \times 10^{-7}$  mol/mol of tBVE at  $-30^\circ\text{C}$ .

## CONCLUSIONS

To effectively prepare isotactic-rich poly(tBVE) with a narrow molecular weight distribution, which is expected to be a promising precursor for isotacticity-rich PVA, tBVE was polymerized in different solvents at various temperatures. The polymerization of tBVE with ansa-zirconocene/ $B(C_6F_5)_3$  was a fast reaction because of the strong interaction between tBVE with a branched substituent and ansa-zirconocene/ $B(C_6F_5)_3$ . The ultimate conversion was obtained within a polymerization time of 10 min at all polymerization temperatures. The conversion into polymer was controlled from 60 to 90% at polymerization temperatures ranging from  $-70$  to  $-10^\circ\text{C}$ , and the maximum was obtained at  $-30^\circ\text{C}$ . The  $M_n$  values of poly(tBVE) were approximately 14,000–20,000 with a polydispersity index of 1.48–1.77 at all polymerization temperatures. The isotactic triad fraction of poly(tBVE) polymerized with ansa-zirconocene/ $B(C_6F_5)_3$  at  $-30^\circ\text{C}$  was much higher than that of poly(tBVE) polymerized with homo- $B(C_6F_5)_3$  at  $-30^\circ\text{C}$ . In the near future, we will report on the preparation of isotacticity-rich PVA by the saponification of poly(tBVE) prepared in this study.

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